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Published in:
Physical Review Letters

DOI:
[10.1103/PhysRevLett.79.5138](https://doi.org/10.1103/PhysRevLett.79.5138)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
1997

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Els, G., Loosdrecht, P. H. M. V., Lemmens, P., Vonberg, H., Güntherodt, G., Uhrig, G. S., Fujita, O., Akimitsu, J., Dhalenne, G., & Revcolevschi, A. (1997). Observation of three-magnon light scattering in CuGeO₃. *Physical Review Letters*, 79(25), 5138 - 5141. <https://doi.org/10.1103/PhysRevLett.79.5138>

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Observation of Three-Magnon Light Scattering in CuGeO_3

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(Received 5 May 1997)

Temperature and magnetic field dependent polarized Brillouin spectra of CuGeO_3 are reported. In addition to a bound singlet state at 30 cm^{-1} , a new feature has been observed at 18 cm^{-1} . This feature is interpreted in terms of a novel three-magnon light scattering process between excited triplet states. [S0031-9007(97)04862-X]

PACS numbers: 75.40.Gb, 75.10.Jm, 75.50.Ee

The unusual properties of low-dimensional antiferromagnetic Heisenberg spin chains, such as the occurrence of the Haldane gap [1], low energy quantum fluctuations and dominant spin-wave continua [2], and the magneto-elastic spin-Peierls (SP) transition [3], have attracted the interest of both experimental and theoretical physicists over the past two decades. Recently, this interest has been boosted once more by the discovery [4] of a SP transition in the inorganic compound CuGeO_3 . This inorganic nature of CuGeO_3 increased tremendously the possibilities for experimental studies of a SP system [5]. These, in turn, intensified the theoretical efforts to understand the properties of CuGeO_3 and of frustrated dimerized $S = 1/2$ antiferromagnetic spin chains in general.

To first approximation, CuGeO_3 is described as a frustrated quasi-one-dimensional $S = 1/2$ isotropic Heisenberg antiferromagnet coupled to the elastic degrees of freedom of the lattice. Because of this coupling, the system undergoes a SP transition at $T_{\text{SP}} = 14\text{ K}$ to a dimerized nonmagnetic ground state. Frustration in this system arises from competing antiferromagnetic nearest-neighbor (nn) and next-nearest-neighbor (nnn) interactions ($J_{\text{nn}} = 120\text{--}160\text{ K}$, $\alpha = J_{\text{nnn}}/J_{\text{nn}} = 0.24\text{--}0.37$ [6–8]). The influence of interchain coupling [9] will be discussed later in this Letter.

The spin-Peierls transition results from the instability of spin-chain systems towards dimerization. The gain in magnetic energy overcompensates the necessary elastic energy $\propto \delta^2$ (δ : dimerization amplitude). For $\alpha < \alpha_c$ ($\alpha_c = 0.241$ [10]), this gain is proportional to $\delta^{4/3}$ [11]. For $\alpha > \alpha_c$ the gain is even linear in δ since the magnetic system in itself already breaks the translational symmetry [10,12]. In this case, the magnetic system also displays a relatively small energy gap Δ_{frus} without lattice dimerization.

Inelastic light scattering (ILS) has proven to be a sensitive technique to study magnetic excitations in CuGeO_3 [13–16]. It is the aim of this Letter to show the existence of a, so far, unobserved type of magnetic scattering process in gapful, low-dimensional spin systems. This scattering process was seen by temperature and magnetic field dependent polarized Brillouin scattering experiments in the SP phase of CuGeO_3 .

The single crystals used in this study were grown by two different groups [17,18] using a traveling floating zone method. We did not note any qualitative differences between crystals from the two sources. The crystals were cleaved along the (100) planes to obtain a virgin surface and mounted in a He flow cryostat (stabilized within $\pm 0.1\text{ K}$). Polarized Brillouin spectra were recorded in a 90° geometry using a Sandercock-type tandem Fabry-Perot spectrometer, with the 514.5 nm line of an Ar^+ laser as the excitation source (incident fluence $\leq 140\text{ W/cm}^2$). Because of the transparency of the CuGeO_3 samples heating effects were estimated to be less than 0.5 K . The advantage of Brillouin spectroscopy is its high contrast close to the laser line. For the experiment presented a particular small mirror spacing of $100\text{ }\mu\text{m}$ is used to achieve the necessary large free spectral range of 50 cm^{-1} . To ease comparison with Raman spectra we choose cm^{-1} as energy scale ($1\text{ cm}^{-1} = 30\text{ GHz} = 0.125\text{ meV}$).

In ILS the opening of the magnetic gap in the SP phase is evidenced by the appearance of a sharp asymmetric peak in the spectrum at about 30 cm^{-1} [13,14]. The appearance of this mode is depicted in Fig. 1(a), which displays (ZZ) polarized Brillouin spectra ($Z \parallel$ chains) for several temperatures in the vicinity of the SP transition. At the lowest temperature a clear, asymmetric, resolution-limited peak is observed at 30 cm^{-1} . With increasing

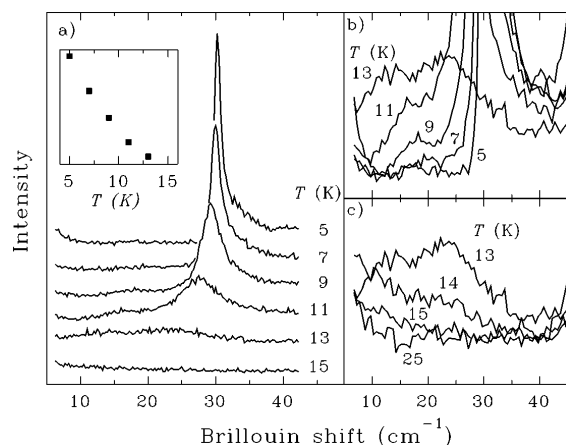


FIG. 1. ZZ polarized Brillouin spectra for several temperatures showing the singlet bound state response (a) (the curves have been given an offset for clarity), a thermally induced low energy scattering process below T_{SP} (b), and the disappearance of the scattering intensity for $T > T_{SP}$ (c). The inset in (a) shows the T dependence of the peak intensity of the singlet bound state response.

temperature the observed peak shifts to lower energies and strongly broadens. This is evidently associated with the closure of the SP gap upon approaching the SP transition at 14 K. The inset of Fig. 1(a) shows the peak intensity of the singlet bound state response as a function of temperature. An extrapolation of the peak intensity beyond 13 K is in good agreement with the SP transition temperature ($T_{SP} = 14$ K).

It is evident from the Brillouin spectra in Fig. 1 that the 30 cm^{-1} mode is not the only low energy excitation. This is more clearly depicted in Figs. 1(b) and 1(c), which show the data on an expanded intensity scale. One observes a low energy shoulder in spectra between T_{SP} and 7 K. The T dependence of the frequency and peak intensity of this shoulder are shown in Figs. 2(a) and 2(b) (filled symbols), respectively. At $T = 13$ K,

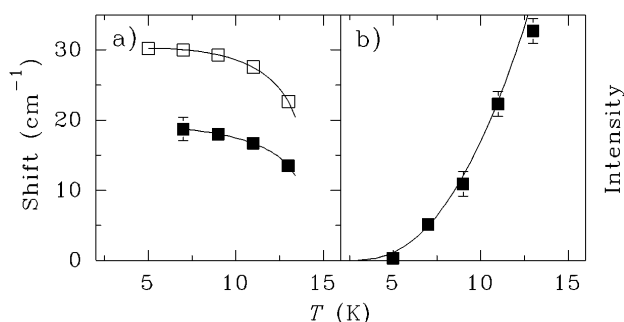


FIG. 2. (a) Temperature dependence of the energy of the singlet bound state (open symbols) and the 18 cm^{-1} (filled symbols) response. Solid lines are guides to the eye. (b) Temperature dependence of the intensity of the 18 cm^{-1} shoulder (filled symbols). The solid line demonstrates the activated T dependence of the intensity of the 18 cm^{-1} response (see text).

the shoulder is found at about 13 cm^{-1} . As T is decreased, it is shifted towards higher energies, but simultaneously loses its intensity until it finally becomes unobservable at about 5 K. Apparently, the T dependence of the frequency of this shoulder is similar to that found for the 30 cm^{-1} singlet bound state response [Fig. 2(a), open symbols]. Furthermore, we did not find any intensity on the anti-Stokes side of the spectra consistent with the thermal suppression of the intensity $I_{\text{anti-Stokes}}/I_{\text{Stokes}} \propto \exp[-\hbar\omega/(k_B T)]$ in this frequency and temperature range.

The unusual T dependence of the intensity of the 18 cm^{-1} shoulder strongly indicates that the scattering process involved is due to transitions between *excited* states. It implies also that this shoulder is distinct from the structure observed in Raman scattering experiments in the same frequency region, but at a rather low temperature, $T = 2$ K, which has tentatively been assigned to one-magnon scattering [16]. We did not find any signature of the latter mode. The shoulder observed here is fully (ZZ) polarized. No scattering intensity could be observed in crossed (ZY) or circular (Z_c) polarization of the scattered light. Also no magnetic field dependence could be found up to 6 T. These facts rule out a one-magnon process which should have an antisymmetric Raman tensor and should display Zeeman splitting.

For a better understanding, let us recall the low lying excitations in dimerized frustrated spin chains (see Fig. 3). For $T > T_{SP}$ we have no dimerization ($\delta = 0$) and, depending on the value of α , Fig. 3(a) [2] or Fig. 3(b) [19] applies. In the dimerized SP phase ($T < T_{SP}$) we have $\delta > 0$, and a gap Δ opens between the singlet ground state and the lowest elementary triplet excitations ($S = 1$, "magnons"). These triplets (Fig. 3, thick solid line) are again separated by a gap Δ from the two-magnon continuum (Fig. 3, shaded area) starting at 2Δ [20]. For δ not too small, there is no qualitative difference between $\alpha < \alpha_c$ and $\alpha > \alpha_c$ [see Figs. 3(c) and 3(d)]. In addition to the $S = 1$ excitations, a well-defined singlet mode is predicted below the continuum [Figs. 3(c) and 3(d), dashed lines] [20,21]. It can be viewed as a singlet bound state of two antiparallel magnons [20]. The energy difference from the continuum onset at 2Δ is its binding energy. Larger dimerization lowers, whereas larger frustration enhances the singlet binding effect [20,22].

The existence of a continuum above T_{SP} in CuGeO_3 is confirmed by Raman [14] and inelastic neutron [23] scattering experiments. The opening of a gap in the magnetic excitation spectrum was experimentally verified in CuGeO_3 using a variety of methods [4,24–26]. First neutron experiments on the magnetic excitation spectrum of CuGeO_3 in the SP phase showed the existence of a single branch of well defined elementary triplet excitations [24]. Recently, inelastic neutron scattering experiments revealed that these elementary triplet excitations

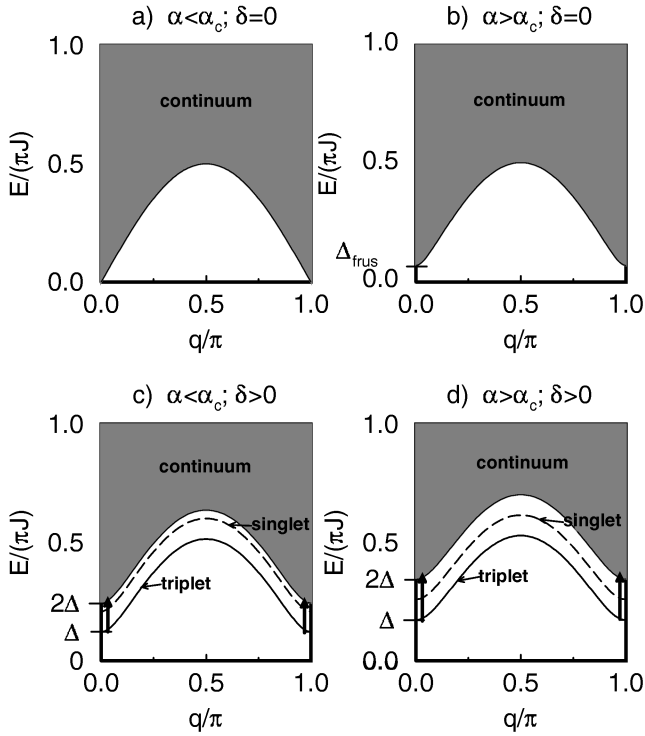


FIG. 3. Schematic representations of the magnetic excitation spectrum expected for a $S = 1/2$ Heisenberg antiferromagnetic chain: with dimerization, (c) and (d); with frustration, (b) and (d). Thin solid line: onset of the continuum of $S = 1$ or $S = 0$ excitations. Shaded area: continuum (no statement on spectral weights is made). Thick solid line: elementary magnon excitation $S = 1$. Dashed line: bound state singlet excitations. The vertical arrows describe the three-magnon scattering (see text).

are separated from a continuum starting at about twice the gap [27]. The singlet bound state below the onset of the continuum is visible in ILS data at 30 cm^{-1} [see Fig. 1(a)] relatively close to the continuum onset [13,14]. Initially, it was suggested that this mode is due to a bound two-magnon state [13]. Other authors [14–16] identified this peak as being due to a direct two-magnon scattering process from the SP gap excitations, based on the near coincidence of this peak with twice the SP gap. Later, however, Raman experiments under pressure confirmed the former hypothesis of a bound two-magnon singlet state, as its binding energy strongly increases upon increasing pressure due to an enhancement of the frustration α [22].

We now propose an explanation for the 18 cm^{-1} shoulder which is consistent with the above observations. Within standard Fleury-Loudon theory [28] for ILS in magnetic solids, the transition operator for a dimerized and frustrated spin chain (see also [29]) is of the type

$$R = \sum_i (1 + (-1)^i \delta) \mathbf{S}_i \cdot \mathbf{S}_{i+1} + \gamma \mathbf{S}_i \cdot \mathbf{S}_{i+2}. \quad (1)$$

This operator R conserves the total spin since it is a scalar. In order to gain insight into possible scattering processes, it

is allowed to work in the limit of strong dimerization with δ close to unity. This point of view has proved to be very useful for a qualitative understanding [9,20]. In this limit the ground state is a product of local singlets at the strong bonds (henceforth called dimers). A magnon excitation consists of one triplet at one of the dimers. Because of the residual weak bonds, these triplets acquire a dispersion. The application of R in (1) on the ground state creates two triplets on adjacent dimers combined to $S = 0$. Thus a light scattering experiment at $T = 0$ probes essentially the two-magnon subspace, displaying a continuum and a bound singlet state below the continuum onset [20].

At finite temperature we may also start from the situation where one magnon is already excited. The application of R at $T \neq 0$ might (i) create two *additional* adjacent triplets somewhere (two-magnon scattering) or (ii) convert one triplet into two adjacent triplets. The latter process is what we call a three-magnon scattering process. Spin conservation requires that these two triplets are combined to $S = 1$.

For illustration, let us consider four spins $\mathbf{S}_1, \mathbf{S}_2, \mathbf{S}_3$, and \mathbf{S}_4 forming two singlets s_{12} and s_{34} . We denote the singlet product as $|s, s\rangle$, omitting the site indices. This state is the ground state for $\delta \rightarrow 1$. We use $R = \mathbf{S}_2 \cdot \mathbf{S}_3$ as the Raman operator with $R = S_2^z S_3^z + (1/2)(S_2^+ S_3^- + S_2^- S_3^+)$. Application of R on $|s, s\rangle$ yields

$$R|s, s\rangle = (1/4)(-|t_0, t_0\rangle + |t_1, t_{-1}\rangle + |t_{-1}, t_1\rangle), \quad (2)$$

where $t_{0,\pm 1}$ denotes the triplet state with the corresponding S^z component. The total spin before and after the application of R is zero. Process (2) creates two elementary magnons and corresponds to the $T = 0$ situation and to process (i) above. If we choose $|t_0, s\rangle$ as the initial state to describe process (ii), the result is

$$R|t_0, s\rangle = (1/4)(-|s, t_0\rangle + |t_1, t_{-1}\rangle - |t_{-1}, t_1\rangle). \quad (3)$$

Here, the total spin before and after the application of R is unity. The first term in (3) does not change the number of magnons in the system. The other terms induce a transition from one to two magnons thus incrementing the number of magnons by one. This is the three-magnon process (ii). Note that this process is lost in any bosonic description (Holstein-Primakov or bond operator) of antiferromagnets, where only the quadratic terms are kept. For this reason, we conclude that the three-magnon process is a generic feature in gapful, low-dimensional spin liquids which are *not* described by Néel-type states.

Treating the magnons like independent bosons, the T dependence of the intensity of the three-magnon process is given by

$$I \propto n(\omega_i)[1 + n(\omega_{f1})][1 + n(\omega_{f2})], \quad (4)$$

where $n(\omega)$ is the Bose distribution function and ω_i, ω_{f1} , and ω_{f2} are the magnon energies of the initial magnon and the two final magnons, respectively. For $T \ll \Delta \approx 23 \text{ K}$, one has $I \propto n(\omega_i)$, which for $T = 0$ vanishes since there are no excited magnons in the system anymore.

Returning to the 18 cm^{-1} response observed in the Brillouin spectra (Fig. 1), we interpret this structure now as the *onset of a continuum* of momentum conserving vertical ($\Delta\vec{q} = 0$) transitions from the lowest magnon branch (thick line in Fig. 3) to the two-magnon continuum of $S = 1$ excitations (shaded area in Fig. 3) [see vertical arrows in Figs. 3(c) and 3(d)]. The three-magnon scattering relies on the same operator R as does the rest of the Brillouin spectrum. It therefore obeys the same selection rules, in excellent agreement with experiment, and conserves the total spin and each spin component. Thus, there is no shift or splitting in a magnetic field as observed experimentally. In view of the low temperatures of the experiments, one expects that the major contribution to the scattered intensity comes from transitions with an initial state which has an energy comparable to the SP gap $\Delta = 2.1\text{ meV}$. The onset of the observed scattering is therefore determined by the energy difference between the onset of the continuum at about $2\Delta = 4.2\text{ meV}$ [27] and the SP gap which is again $\Delta = 2.1\text{ meV}$. This is in good agreement with the data in Fig. 1. The temperature dependence of the intensity at 18 cm^{-1} [Fig. 2(b)] is also found to agree well with the expected dependence (4). This is shown in Fig. 2(b) by the solid line which is calculated using $\omega_i = \omega_{f1} = \omega_{f2} = \Delta = 2.1\text{ meV}$. Since the softening of the 18 cm^{-1} structure follows the same behavior as both the singlet bound state response and the spin-Peierls gap [see Fig. 2(a)], one may conclude that all excitations depicted in Fig. 3 renormalize in the same manner until they merge with the continuum of the uniform isotropic $S = 1/2$ Heisenberg antiferromagnet [2,14,23] at the phase transition.

So far, we have discussed the energies of the three-magnon process in CuGeO_3 on the basis of a $d = 1$ model. In order to demonstrate that the interchain coupling does not change the picture qualitatively, we refer to the $d > 1$ dispersion calculated in Ref. [9] (see Fig. 4 therein). If we start from the magnon at the zone center $\vec{q}_i = (0,0,0)$ with $\omega_i = 2.5\text{ meV}$, we may induce a momentum conserving transition to the magnons with minimum energy $\omega_{f1} = \omega_{f2} = \Delta = 2.1\text{ meV}$ at $\vec{q}_{f1} = (0,1,1/2)$ and at $\vec{q}_{f2} = -\vec{q}_{f1}$. This leads to an onset at $2 \times 2.1 - 2.5 = 1.7\text{ meV}$ or 14 cm^{-1} . All transitions at other points in the Brillouin zone lead to larger values for the onset. Inspection of Fig. 1 shows that the onset at 14 cm^{-1} is also (perhaps even better) compatible with the experiment. Thus, our explanation is not restricted to the (simplified) $d = 1$ picture of CuGeO_3 .

In conclusion, we have reported on a low energy transition in CuGeO_3 observed in Brillouin scattering. This transition is assigned to a novel three-magnon scattering process between the lowest triplet branch and the continuum of triplet states in CuGeO_3 , in excellent agreement with the experimental results for energy, temperature dependence, magnetic field dependence, and polarization se-

lection rules. The three-magnon process is expected to be a generic feature in gapful, low-dimensional spin systems.

We are grateful for helpful discussions with G. Bouzerar, P. Fumagalli, B. Hillebrands, J.R. Sandercock, F. Schöfneld, and M. Udagawa. This work was supported by the DFG through SFB 341 and by the BMBF Fkz. 13N6586/8. Laboratoire de Chimie des Solides is a "Unité de Recherche Associée CNRS No. 446."

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